Band Theory and Electronic Properties of Solids

Phys 674

Physics & Astronomy
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Week No. 03

The Sommerfeld Theory of Metals Part I

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The Sommerfeld Theory of Metals

the Sommefeld theory of metals:

major works of Sommerfeld:

① Development of Quantum Theory

- * he Introduced Bohr-Sommerfeld model
  In this model orbits are elliptical
- * Fine structure of Hydrogen atom.
  He used relativistic corrections.

② Atomic Spectra & Zeeman Effect:

- * He clarified the influence of mag. field on Energy levels.
- * He explained the "Anomalous Zeeman Effect"
  for this he introduced the spin of electron.

The Sommerfeld Theory of Metals

③ His Role in Electrodynamics:

he has lots of work on diffraction and wave propagation

④ His work on "Fermi-Sommerfeld theory of metals"

in this work he applied Q.M. to explain the electronic properties of metals (the free electron model)

⑤ in statistical mechanics:

he extended Maxwell-Boltzmann statistics → Fermi-Dirac and Bose-Einstein "

The Sommerfeld Theory of Metals

Introduction

① during Drude time there was only Classical Distribution methods.

$$f(x) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m x^2}{2 k_B T}}$$

max-Boltz.dis.
-- (2.1)

$\Longrightarrow$ 1 e Contribute $\frac{3}{2}k_B$ to C_v

this does not agree with exp.

② Contradiction Between Drude Model and exp. in specific heat Continued 25 years

③ it was only Resolved after Quantum was Establishe

④ Maxwell-Boltzmann distribution was Replaced

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6.5. Fermi Dirac Distribution

$$f(\epsilon) = \frac{1}{e^{\frac{(\epsilon-\mu)}{k_B T}}+1} \quad --- (2.2)$$

⑤ this distribution is totally different than M-B in its results

⑥ Pauli exclusion principle was established for electron states in atoms.
S.F. used it for the free electron gas of Metals.
⇒ solution to the most big thermal anomalies of the Drude model.

⑦ in many cases S.F model is nothing but Drude model with single modifications.

The Sommerfeld Theory of Metals

electron velocity distribution is based on
F. Dirac dist. instead of Max.-Bol.

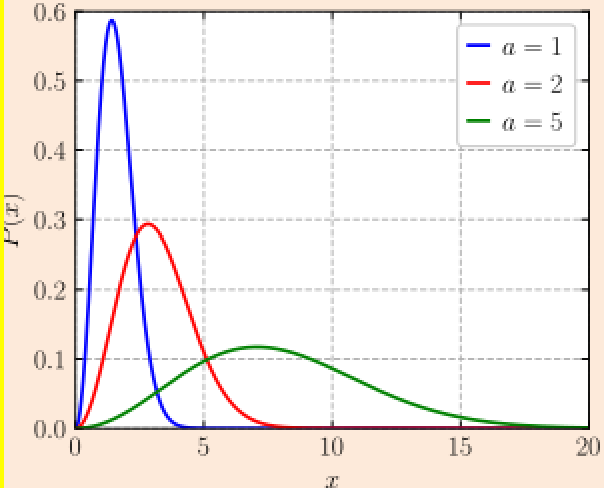
The Sommerfeld Theory of Metals

Introduction

- In Drude's time, and for many years thereafter, it seemed reasonable to assume that the electronic velocity distribution. like that of an ordinary classical gas of density n = *N/V,* was given in equilibrium at temperature *T* by the Maxwell-Boltzmann distribution:

$$f_B(v) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT} \qquad (2.1)$$

- This distribution predicts a contribution to the specific heat of a metal of $\frac{3}{2}k_B$ per electron that contradicts with experimental data. We have seen in chapters 5&6 of Kittel that specific heat is temperature dependent.



Introduction

- Contradiction between values of specific heat based on Drud’s model and experiment continued for about 25 years. It was only resolved after recognizing that electrons do participate and that Pauli Ex. Principle play its role.
- This forced scientists to replace the Maxwell-Boltzmann distributing with Fermi-Dirac distribution

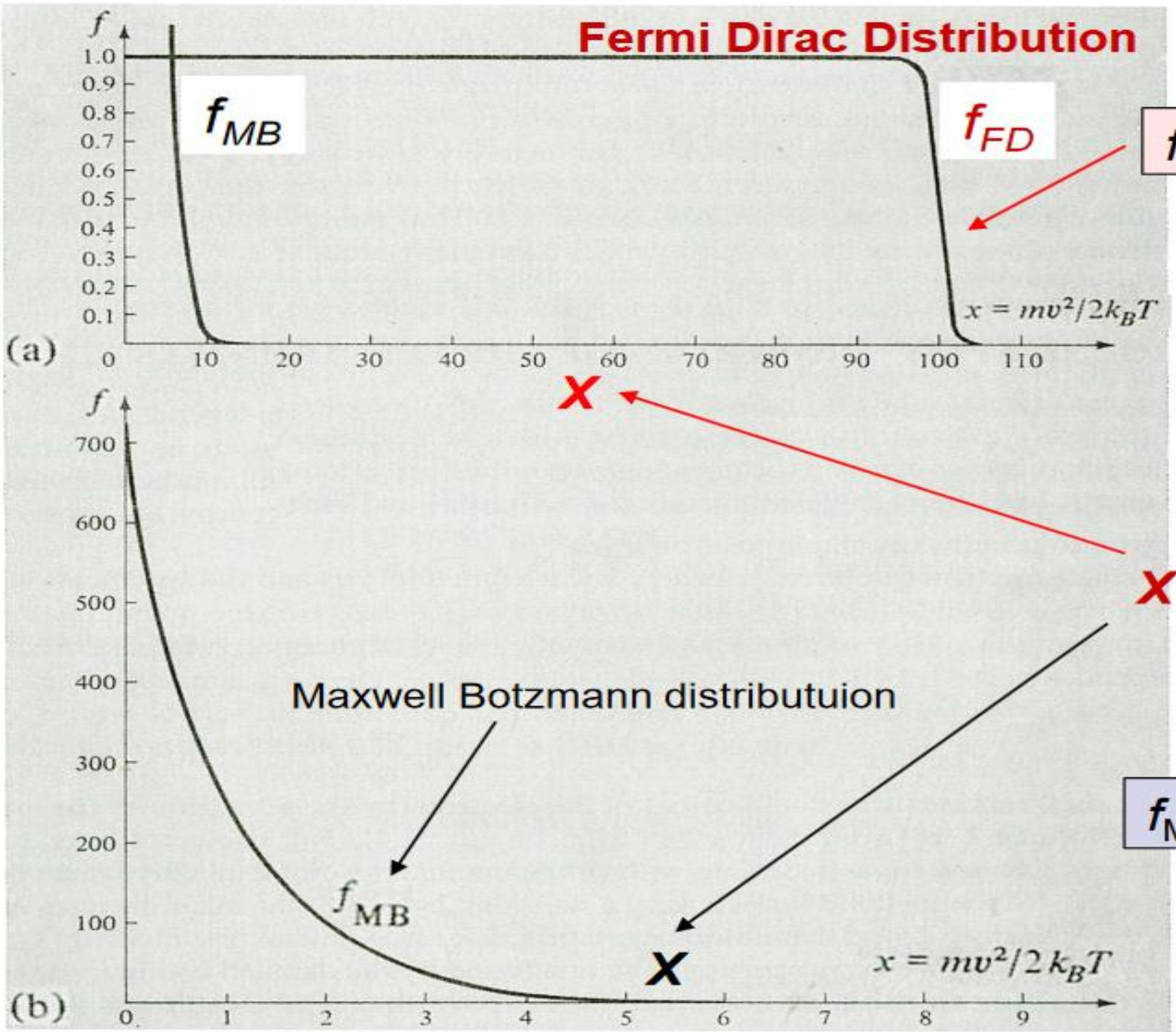
$$f(v)=\frac{(m/\hbar)^3}{4\pi^3}\frac{1}{e^{\left(\frac{1}{2}mv^2-k_BT_o\right)/k_BT}+1} \qquad (2.2)$$

$$OR: f(\varepsilon)=\frac{1}{e^{\left[(\varepsilon-\mu)/k_BT\right]}+1}$$

- At temperatures of interest (that is less than 10^3 K) the Maxwell-Boltzmann and Fermi-Dirac distributions are completely different at metallic electronic densities.
- In this chapter we shall relay on the Fermi-Dirac distribution

The Sommerfeld Theory of Metals

Introduction



$f_{FD} = [exp(x) + 1]^{-1}$

$X = m\upsilon^2/2K_BT$

$f_{MB} \propto v^2 \exp(-mv^2/2K_BT)$

Introduction

❑ Shortly after the discovery that the *Pauli exclusion principle* was needed to account for the bound electronic states of atoms, Sommerfeld applied the same principle to the free electron gas of metals, and thereby resolved the most big thermal anomalies of the early Drude model.

❑ In most applications Sommerfeld's model is nothing more than Drude's classical electron gas with the *single* modification that the electronic velocity distribution is taken to be the quantum Fermi-Dirac distribution rather than the classical Maxwell-Boltzmann distribution

❑ For simplicity we shall examine the ground state (i.e., T = 0) of the electron gas before studying it at nonzero temperatures.

❑ Then we proceed with Sommerfeld theory.

② in our first test of the S.F. Model we will use it at T=0 (ground state)

③ please Read the slides about N electrons in a box

$$\Rightarrow \mathcal{E}_k = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) \quad \cdots\cdots (2.9)$$

to understand this equation:

* you have to use Reciprocal space (k-sp)

* in K-space: each point ≡ wavevector $\vec{K}$

* $\bar{K}$ ≡ momentum of the particle

* K in K-space is quantized

$$K_x = \frac{2\pi n_x}{L} \qquad K_y = \frac{2\pi n_y}{L}$$

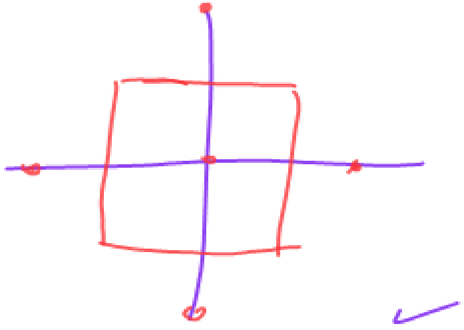
* why K must be quantized?

Because wave function must satisfy Perriodicity OR Boundary Conditions.

* Let us have "one point" in K-space in 2D

$\Rightarrow$ Area of this point

$$= \frac{2\pi}{L} \times \frac{2\pi}{L} = \left(\frac{2\pi}{L}\right)^2$$



in 3D $\Rightarrow$ volume $= \left(\frac{2\pi}{2}\right)^3$

$$= \frac{8\pi^3}{V}$$

∴ one point $\longrightarrow \frac{8\pi^3}{V}$

$\Rightarrow$ density $= \frac{V}{8\pi^3}$ (density of points)

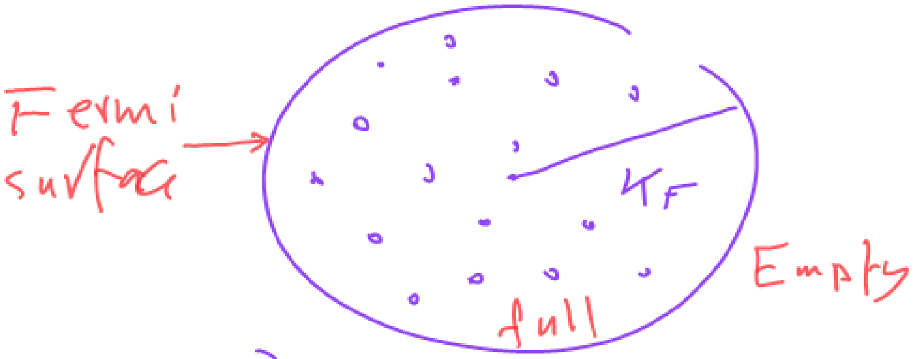
≡ " " Levels)

≡ " " states)

* if we have a sphere with Radius K_F

this is Fermi sphere

Volume $= \frac{4}{3}\pi K_F^3$



$\Rightarrow$ Number of values:

$$N = \frac{\frac{4}{3}\pi K_F^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{\frac{\cancel{4}}{3}\cancel{\pi}K_F^3}{\text{②}\cancel{8}\,\pi^{\text{③}2}}\cdot V = \frac{K_F^3}{6\pi^2}V$$ ##

* N is the total No. of states inside the sphere

* But Pauli ex. princ. allow 2:

$$\therefore N = \frac{K_F^3}{6\pi^2} V \times 2 = \frac{K_F^3}{3\pi^2} V \quad \#$$

* sinc Every state has 2 electrons.

∴ N is the No. of electrons inside the Fermi sphere.

* Ground state of N electron:

≡ all of N being inside the sphere

* density of electrons $= n = \frac{N}{V}$

∴ $n = \dfrac{k_F^3}{3\pi^2}$

∴ eq. (2.9) $\rightarrow$ $\varepsilon_F = \dfrac{\hbar^2 k_F^2}{2m}$

④ "Fermi surface is a fundamental " properties of modern theory of metals"

$\hbar k_F$: Fermi momentum

$\varepsilon_F = \dfrac{\hbar^2 k_F^2}{2m}$ " Energy

$v_F = \dfrac{\hbar k_F}{m}$ " velocity.

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

❑ We must calculate the ground-state properties of *N* electrons confined to a volume *V* using independent electron approx.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_k(r)=\varepsilon_k\psi_k(r) \qquad (2.3)$$

Let the volume:

$$V = L^3$$

Applying B.C.

$$\left.\begin{aligned}\psi(x+L,y,z)&=\psi x,y,z)\\ \psi(x,y+L,z)&=\psi x,y,z)\\ \psi x,y,z+L)&=\psi(x,y,z)\end{aligned}\right\} \qquad (2.4)$$

❑Equation (2.4) is known as the *Born-von Karman* (or periodic) *boundary condition*.

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- ❑ Solution to (2.3) is of the form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \mathrm{e}^{i\mathbf{k}.\mathbf{r}} \qquad (2.5)$$

with:

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} \qquad (2.6)$$

- ❑ Wave (2.5) fulfills the conditions:

$$\left.\begin{array}{l} k_x = 0\,, \quad \pm\frac{2\pi}{L}\,, \quad \pm\frac{4\pi}{L}\,, \quad \pm\frac{6\pi}{L}\,, \; ..... \\ k_y = 0\,, \quad \pm\frac{2\pi}{L}\,, \quad \pm\frac{4\pi}{L}\,, \quad \pm\frac{6\pi}{L}\,, \; ..... \\ k_z = 0\,, \quad \pm\frac{2\pi}{L}\,, \quad \pm\frac{4\pi}{L}\,, \quad \pm\frac{6\pi}{L}\,, \; ..... \end{array}\right\} \qquad (2.7)$$

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- ☐ Hence, $k = \frac{2\pi n}{L}$ fulfills the b.c. over L
- ☐ As an example of testing:

$$\mathrm{e}^{\mathrm{i}\mathbf{k}_x\,(\mathrm{x}+\mathrm{L})} = \mathrm{e}^{\mathrm{i}\frac{2n\pi}{L}(\mathrm{x}+\mathrm{L})} = \mathrm{e}^{\frac{\mathrm{i}2n\pi}{L}x}\,\mathrm{e}^{\mathrm{i}2n\pi} = \mathrm{e}^{\frac{\mathrm{i}2n\pi}{L}x}.1 \qquad (2.8)$$

$$= \mathrm{e}^{\mathrm{i}\mathbf{k}_x\,\mathrm{x}}$$

Put (2.5) in (2.3):

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{r}} = \varepsilon_k\ \mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{r}}$$

$$\rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\mathrm{e}^{\mathrm{i}(k_x x+k_y y+k_z z)} = \varepsilon_k\ \mathrm{e}^{\mathrm{i}(k_x x+k_y y+k_z z)}$$

$$\rightarrow \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)\mathrm{e}^{\mathrm{i}(k_x x+k_y y+k_z z)} = \varepsilon_k\ \mathrm{e}^{\mathrm{i}(k_x x+k_y y+k_z z)}$$

$$\therefore \varepsilon_k = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) \qquad (2.9)$$

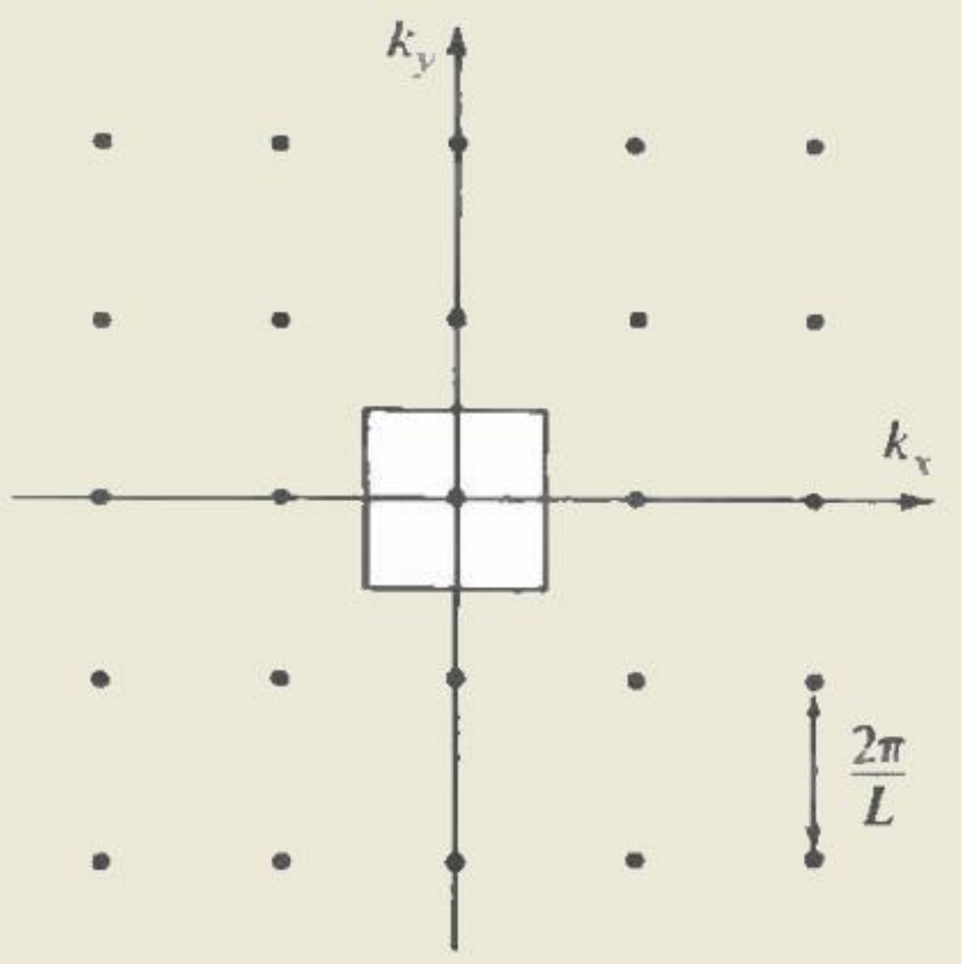
The Sommerfeld Theory of Metals

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- ☐ Points in a two-dimensional k-space of the form $k_x = \frac{2\pi n}{L}$ and $k_y = \frac{2\pi n}{L}$. Note that the area per point is just $\left(\frac{2\pi}{L}\right)^2$.
- ☐ Hence, the allowed k-values per unit volume of k-space (also known as the k-space density of levels) is just:

$$\left(\frac{2\pi}{L}\right)^{-3} = \frac{L^3}{8\pi^3} = \frac{V}{8\pi^3} \qquad (2.10)$$

We consider a Fermi Sphere that has a radius of k_F.



The Sommerfeld Theory of Metals

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- ☐ Hence, *the number of allowed values* of **k** within the Fermi sphere is = (Volume of the Fermi Sphere) ÷(volume of one state)

$$= \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{k_F^3}{6\pi^2} V \qquad (2.11)$$

Thus total no. of states we have (applying Pauli Ex. Princ.):

$$N = 2 \times \frac{k_F^3}{6\pi^2} V \qquad (2.12)$$

- ☐ Thus if *we* have *N* electrons in a volume (density *n* = N/V*)*, then the ground state of the N-electron system is formed by occupying all single particle levels with *k* less than k_F, and leaving all those with *k* greater than k_F unoccupied, where k_F is given by the condition:

$$n = \frac{k_F^3}{3\pi^2} \qquad (2.13)$$

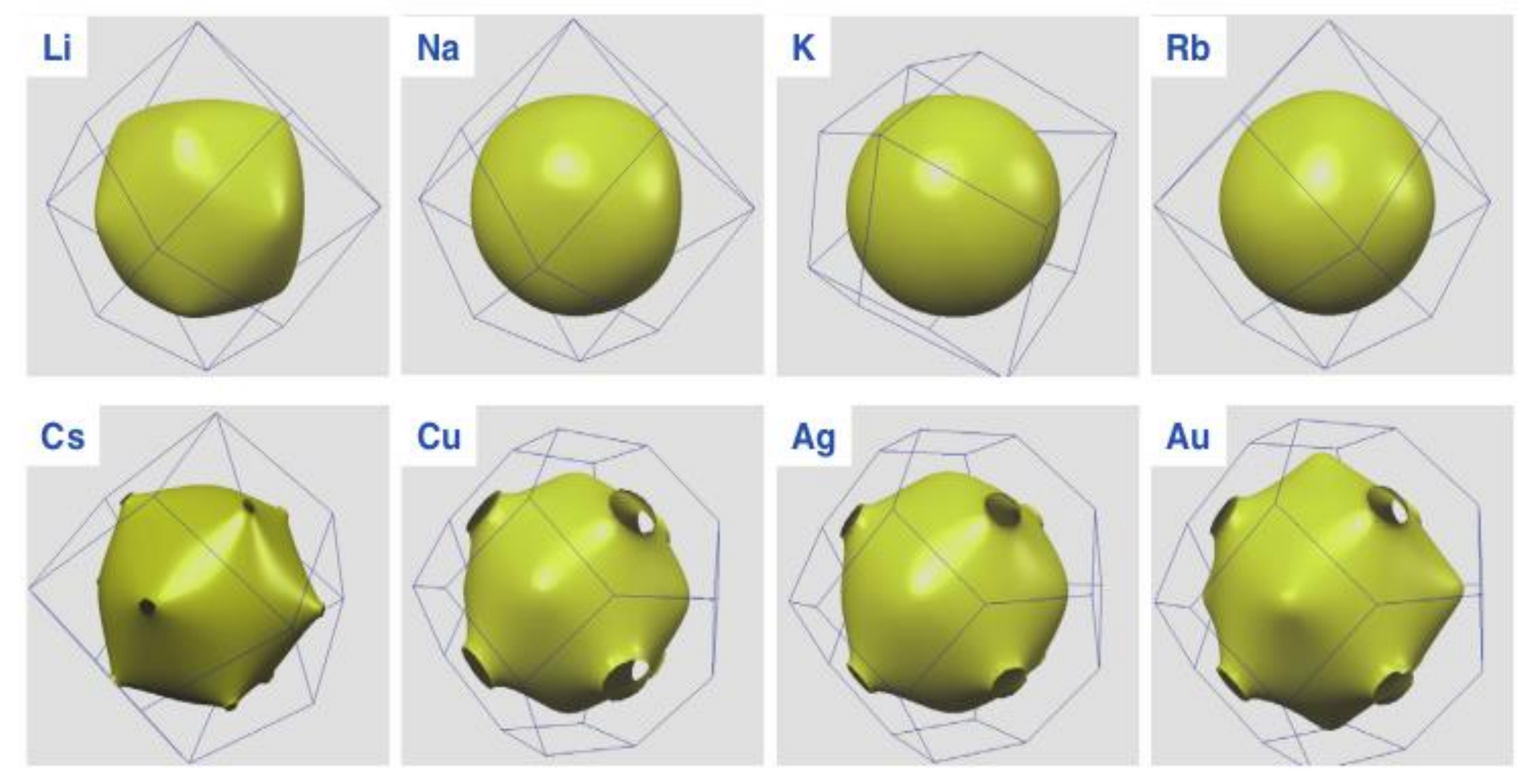
The Sommerfeld Theory of Metals

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- ☐ The sphere of radius k_F containing the occupied one electron levels is called the *Fermi sphere.*
- ☐ The surface of the Fermi sphere, which separates the occupied from the unoccupied levels is called the *Fermi surface.*
- ☐ *The Fermi surface is one of the fundamental constructions in the modern theory of metals. (in general it is not spherical)*
- ☐ The momentum $\hbar k_F = p_F$ of the occupied one-electron levels of highest energy is known as the *Fermi momentum.*
- ☐ Their energy, $\varepsilon_F = \hbar^2 k_F^2/2m$ is the *Fermi energy.*
- ☐ And their velocity, $v_F = p_F/m$, is the *Fermi velocity.*
- ☐ The Fermi velocity plays a role in the theory of metals comparable to the thermal velocity, $v = (3k_B T/m)^{1/2}$ in a classical gas.
- ☐

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

❑ Fermi surfaces of some Alkali metals.



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GROUND-STATE PROPERTIES OF THE ELECTRON GAS

⑤ note that Fermi sphere is too much simplified

⑥ you can tell why Drude model succeeded with Li (spherical)
But not with Cu (non-spherical)
in Li ... etc all electrons are s-state

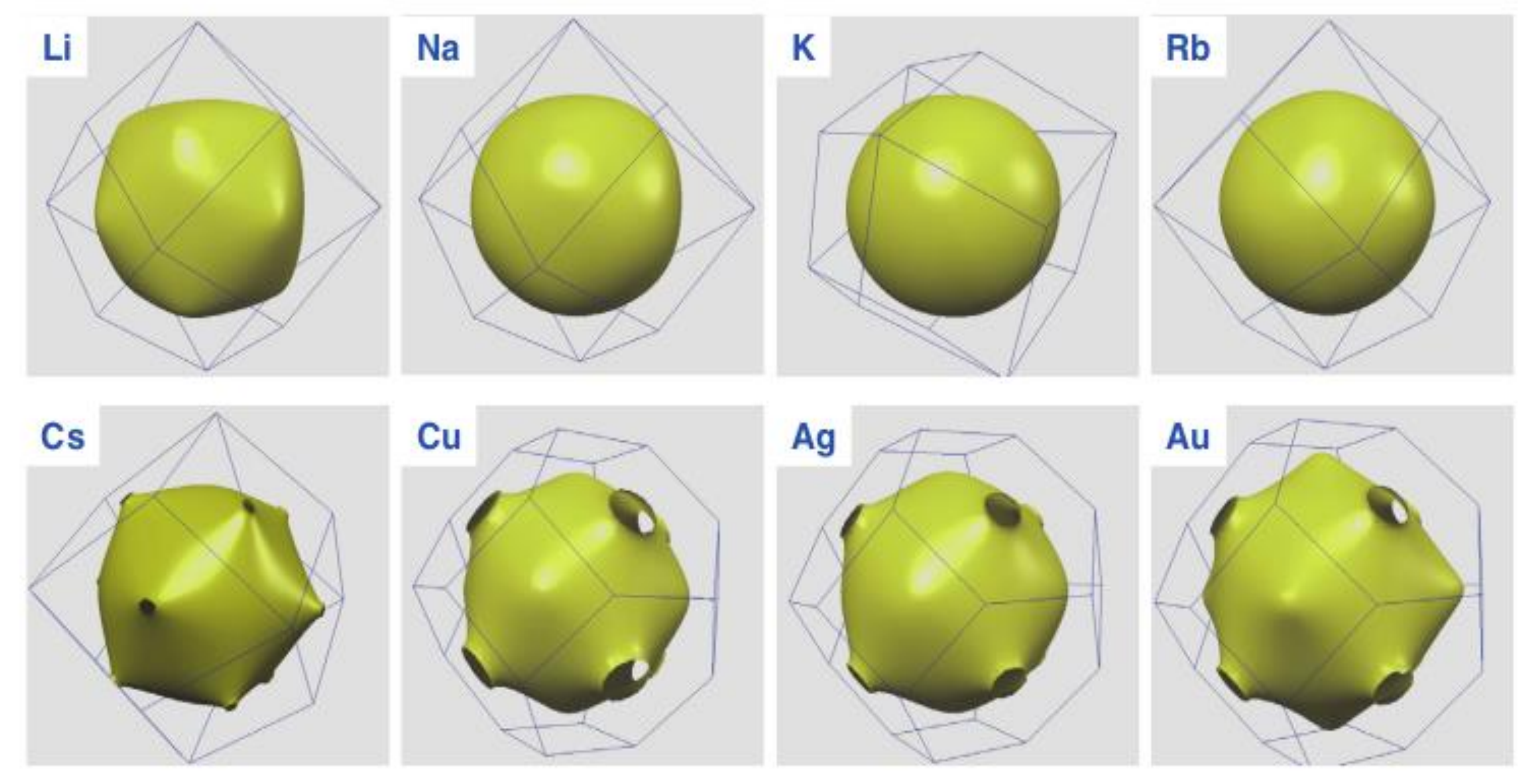
---

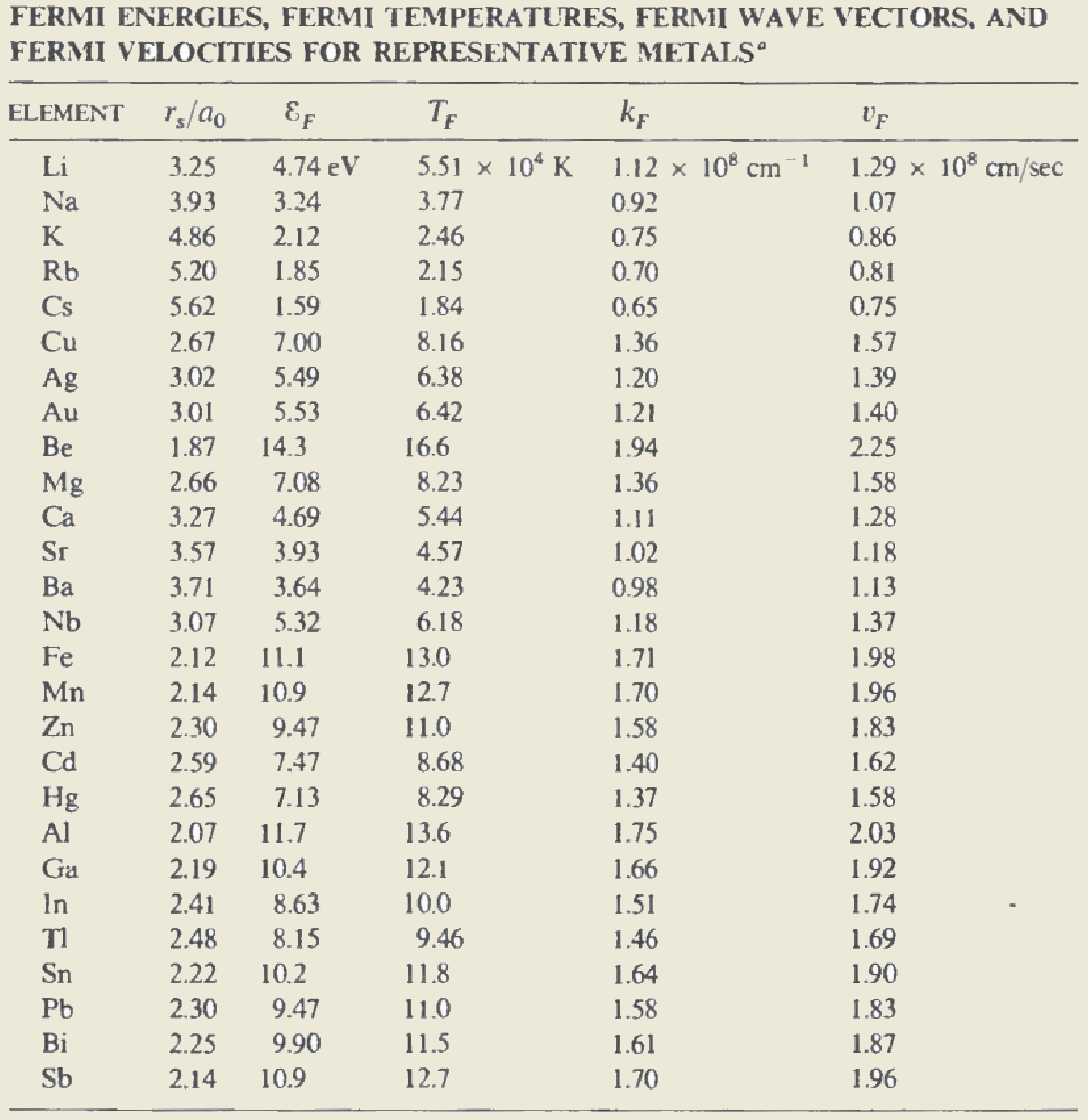
⑦ why we have these "Necks" in Cu, Au, As...
they happen due to strong interaction of conduction electrons with crystal lattice.

The Sommerfeld Theory of Metals

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- ☐ Fermi surfaces of some Alkali metals.





FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS[a]

ELEMENT	r_s/a_0	$\mathcal{E}_F$	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	$1.12 \times 10^8\ \text{cm}^{-1}$	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

Ground state properties of the e-Gas

① let us assume N electrons inside Fermi sphere $K < K_F$

② Total Energy E is :

$$E = 2 \sum_{K<K_F} \frac{\hbar^2}{2m} K^2 \qquad ---\ (2.14)$$

2 is due to Two spin states.

③ let $\frac{\hbar^2}{2m} K^2 \equiv F(\bar{K})$

and $\Delta K = \frac{8\pi^3}{V}$ (size of smallest Volume in K-space)

④ $$\Rightarrow \sum_{k} F(k) = \frac{V}{8\pi^3} \sum F(k)\, \underline{\underline{\Delta k}} \qquad (2.15)$$

Cancel each other

⑤ if V is Large $V \to \infty$

$$\to \sum \to \int$$

$$\therefore \sum_{k} F(k)\Delta k \to \int F(k)\, d^3k$$

$$\therefore (2.15) \to \lim_{V\to\infty} \frac{1}{V} \sum F(k) = \int \frac{d\bar{k}}{8\pi^3} F(k) \qquad --(2.16)$$

⑥ (2.14) $\Rightarrow$

$$\frac{E}{V} = \frac{1}{4\pi^3}\int d\bar{k}\, \frac{\hbar^2 k^2}{2m}$$

$$= \frac{\hbar^2}{8m\pi^3}\int d\bar{k}\; k^2$$

$$= \frac{\hbar^2}{8m\pi^3}\int k^2 (k^2 \sin\theta\, d\theta\, d\phi\, dk)$$

$$= \frac{\hbar^2}{8m\pi^3}\int \underbrace{\sin\theta\, d\theta\, d\phi}_{=4\pi} \int k^4 dk$$

$$= \frac{\hbar^2}{\underset{\textcircled{2}}{\cancel{8}}\, m\pi^{\textcircled{3}}} \cdot \underset{\textcircled{2}}{\cancel{4\pi}} \cdot \frac{k_F^5}{5}$$

$$\therefore\; \frac{E}{V} = \frac{1}{\pi^2}\cdot \frac{\hbar^2 k_F^5}{10m} \qquad (**)$$

⑦ To find Energy/e $= \frac{E}{N}$

we devide by $\frac{N}{V} = n$

$$\therefore \frac{\frac{E}{V}}{\frac{N}{V}} = \frac{E}{V} \times \frac{V}{N} = \frac{E}{N} = \frac{1}{\cancel{\pi^2}} \frac{\hbar^2 k_F^{\overset{2}{5}}}{10m} \div \frac{\cancel{k_F^3}}{3\cancel{\pi^2}}$$

$$\therefore \frac{E}{N} = \frac{3}{5} \cdot \frac{\hbar^2 k_F^2}{2m}$$

$$\therefore \frac{E}{N} = \frac{3}{5} \cdot \epsilon_F \quad ---- (2.16)$$

$$= \frac{3}{5} k_B T_F$$

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

☐ To calculate *the ground-state energy of N electrons* in a volume *V* we must add up the energies of all the one-electron levels inside the Fermi sphere:

$$E = 2\sum_{k<k_F} \frac{\hbar^2}{2m} k^2 \qquad (2.14)$$

☐ We need to do summing of F(**k**) over all values of **k**

☐Because the volume of k-space per allowed **k** value is:$\Delta\boldsymbol{k} = \frac{8\pi^3}{V}$

$$\sum_{k} F(\mathbf{k}) = \frac{V}{8\pi^3}\sum_{k} F(\mathbf{k})\Delta\mathbf{k} \qquad (2.15)$$

☐ for in the limit as $\Delta\boldsymbol{k} \rightarrow 0(V \rightarrow \infty)$ the sum $\sum F(\boldsymbol{k})\Delta\boldsymbol{k}$ approaches the integral ∫ F(**k**)*d**k***:

$$\lim_{V\rightarrow\infty}\frac{1}{V}\sum_{k} F(\mathbf{k}) = \int \frac{d\mathbf{k}}{8\pi^3} F(\mathbf{k}) \qquad (2.16)$$

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- From Eq. (2.16) in Eq. (2.14): We find *the energy density of the electron gas*:

$$\frac{E}{V}=\frac{1}{4\pi^3}\int d\mathbf{k}\,\frac{\hbar^2k^2}{2m}=\frac{1}{4\pi^3}\frac{\hbar^2}{2m}\int d\mathbf{k}k^2=\frac{1}{4\pi^3}\frac{\hbar^2}{2m}\int(k^2 sin\theta d\theta d\phi dk)k^2$$

$$\frac{1}{4\pi^3}\frac{\hbar^2}{2m}\int sin\theta d\theta d\phi\int k^2dkk^2=\frac{1}{4\pi^3}\frac{\hbar^2}{2m}(4\pi)\frac{k_F^5}{5}$$

$$=\frac{1}{\pi^2}\frac{\hbar^2k_F^5}{10m}$$

- To find *the energy per electron*, E/N, in the ground state, we must divide this by N/V:

$$\frac{E}{N}=\frac{1}{\pi^2}\frac{\hbar^2k_F^5}{10m}\div\frac{k_F^3}{3\pi^2}=\frac{3\hbar^2k_F^2}{10m}=\frac{3}{5}\varepsilon_F$$

$$\rightarrow\frac{E}{N}=\frac{3}{5}k_BT_F \qquad (2.16)*$$

⑧ To find the Pressure of Electron Gas:

∵ $P = -\frac{\partial E}{\partial V}$ ----- ①

(2.16) ⇒ ∵ $E = \frac{3}{5} N \epsilon_F$ —— ②

∵ No. of states / unit volume (≡ density)

$= \frac{V}{8\pi^3}$

∴ $N = \frac{V}{\text{②}\,\cancel{8}\,\pi^{\cancel{\text{③}}\,2}} \cdot \frac{\cancel{4}\,\cancel{\pi}}{3} k_F^{3}$ ③ (total No. of states)

∵ $\frac{4}{3}\pi k_F^{3}$ ≡ volume of Fermi sphere

③ → $k_F^{3} = \frac{3N\pi^2}{V}$ - ④ (2 was Cancelled for spin issue)

④ in ②:

$$E = \frac{3}{5} N \cdot \frac{\hbar^2 k_F^2}{2m} = \frac{3}{5} \cdot N \frac{\hbar^2}{2m} \left(\frac{3N\pi^2}{V} \right)^{2/3} \cdots ⑤$$

$$\therefore P = -\frac{\partial E}{\partial V} = -\frac{3}{5} \cdot N \cdot \frac{\hbar^2}{2m} (3N\pi^2)^{2/3} \frac{\partial}{\partial V} (V)^{-2/3}$$

$$= \cancel{-} \frac{\cancel{3}}{5} \cdot N \cdot \frac{\hbar^2}{\cancel{2}m} (3N\pi^2)^{2/3} \left(\cancel{-} \frac{\cancel{2}}{\cancel{3}}\right) (V)^{-5/3}$$

$$= \cancel{N} \cdot \frac{\hbar^2}{5m} \frac{(3N\pi^2)^{5/3}}{3\cancel{N}\pi^2} \left(\frac{1}{V}\right)^{5/3}$$

$$= \frac{\hbar^2}{5m} \frac{1}{3\pi^2} \left(\frac{3N\pi^2}{V} \right)^{5/3}$$

$$\therefore \boxed{P = \frac{2}{3} \cdot \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}} \; - - - - ⑥ \qquad \#$$

The Sommerfeld Theory of Metals

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

❑ One can calculate *the pressure exerted by the electron gas* from the relation: $P=-(\partial E/\partial V)_N$

$$P=-\left(\frac{\partial E}{\partial V}\right)$$

$$\text{using: } E=\frac{3}{5}N\varepsilon_F \;\;\&\;\; \varepsilon_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\Rightarrow E=\frac{3}{5}N\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\Rightarrow P=\frac{2}{3}\frac{E}{V}$$

$$\Rightarrow P=\frac{2}{3}.\frac{1}{\pi^2}\frac{\hbar^2 k_F^5}{10m}$$

⑨ to Find Compressibility and Bulk modulus

K $\qquad$ B

(Prove)

$$\because B = \frac{5}{3} P = \frac{2}{3} \frac{N}{V} \varepsilon_F \quad --- ⑦$$

$$\Rightarrow K = \frac{1}{B} = \frac{3}{2} \frac{V}{N} \frac{1}{\varepsilon_F} \quad --- ⑧$$

The Sommerfeld Theory of Metals

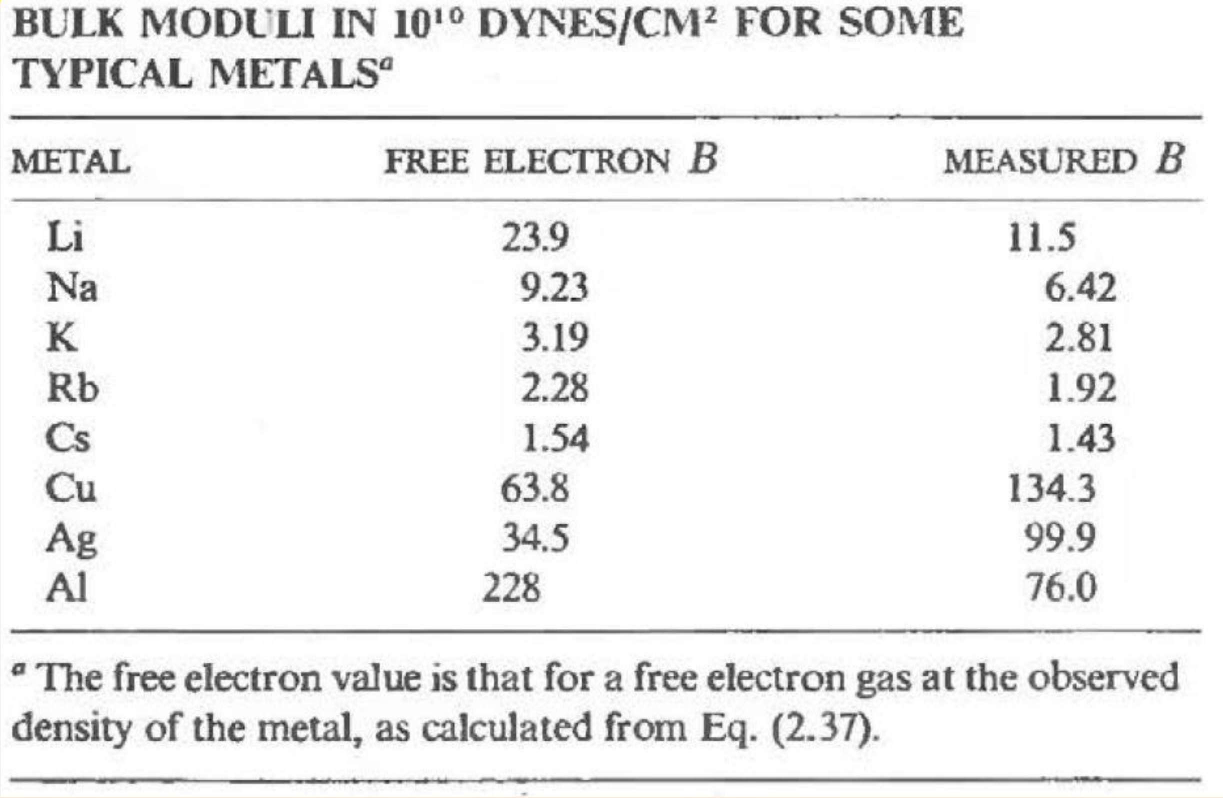
GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- *Compressibility*, K, can be derived as well:

$$B = \frac{1}{K} = -V\left(\frac{\partial P}{\partial V}\right)$$

$$\Rightarrow B = \frac{5}{3}P = \frac{2}{3}\frac{N}{V}\varepsilon_F$$

- Please prove the above relation.
- *B is called Bulk modulus*



BULK MODULI IN 10^{10} DYNES/CM^2 FOR SOME TYPICAL METALS[a]

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

[a] The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

The Figure is our First test of the FEM:

We see that FEM Also fails in B calculation

But its failure is more as the atomic size increases.

Compare Li or Na with AL.

why it fails?

① it did not account for ionic core Interact.

② in large atoms such as Cu, Ag ...

d-electrons interact strongly with lattice

③ it ignores Bonding Contribution..

AL has Covalent Bonding $\Longrightarrow$ increase of B

④ FEM did not include any effect of Bonding at all.

⑤ Crystal lattice Contribution:
Lattice is very important when it comes to B-Modulus.
for instance FCC has more stiffness than BCC.
the FEM has no Consideration of all of that.

⑥ FEM: did not include e-e Interaction
the model (like Drude) did not include any e-e interactions.

⑦ FEM: it assumes uniform density of states for electrons.

this is valid only to s-electrons.

for d-states: density is not uniform

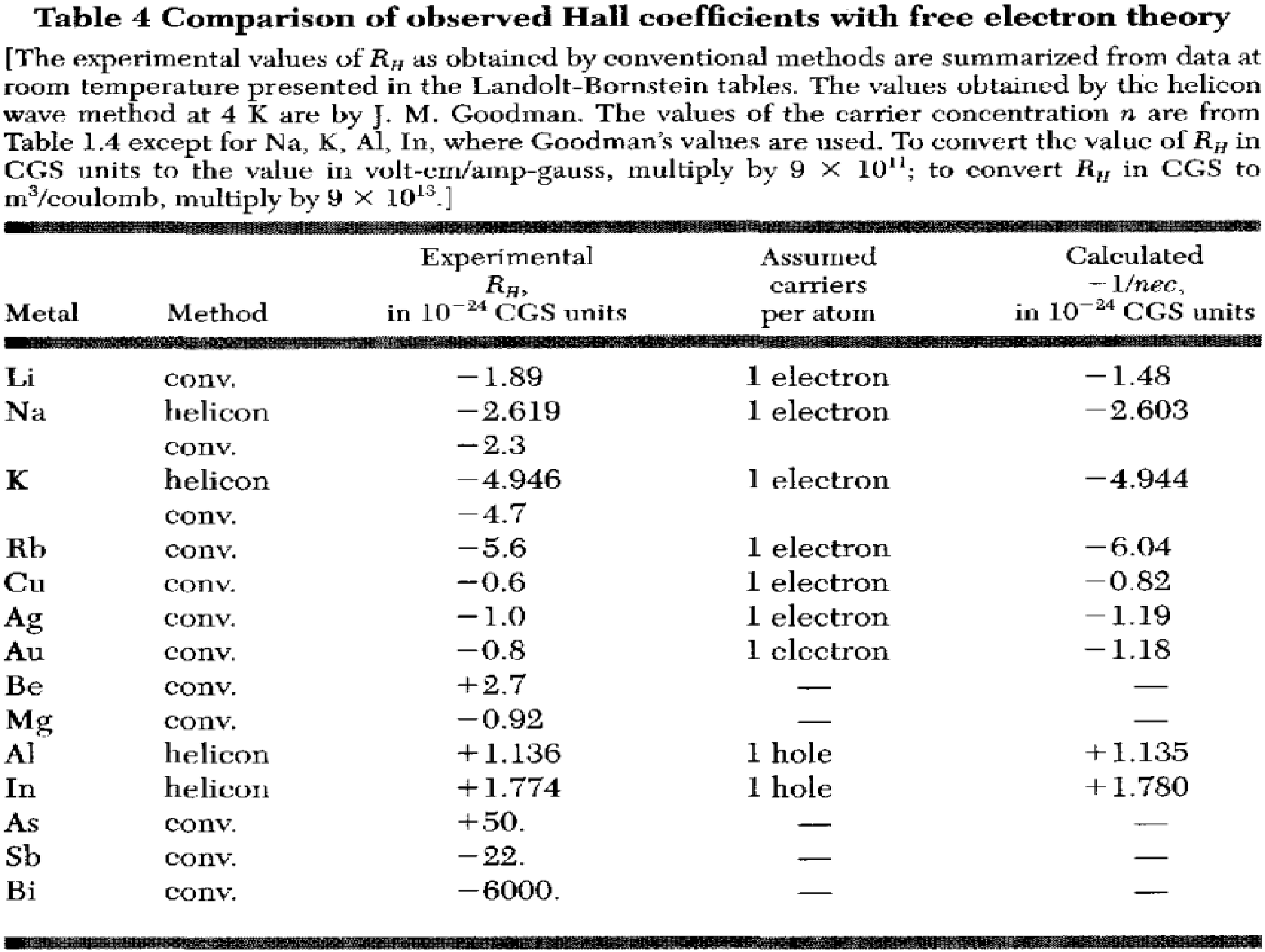


Table 4 Comparison of observed Hall coefficients with free electron theory

[The experimental values of R_H as obtained by conventional methods are summarized from data at room temperature presented in the Landolt-Bornstein tables. The values obtained by the helicon wave method at 4 K are by J. M. Goodman. The values of the carrier concentration n are from Table 1.4 except for Na, K, Al, In, where Goodman's values are used. To convert the value of R_H in CGS units to the value in volt-cm/amp-gauss, multiply by 9×10^{11}; to convert R_H in CGS to m^3/coulomb, multiply by 9×10^{13}.]

Metal	Method	Experimental R_H, in 10^{-24} CGS units	Assumed carriers per atom	Calculated $-1/nec$, in 10^{-24} CGS units
Li	conv.	−1.89	1 electron	−1.48
Na	helicon	−2.619	1 electron	−2.603
	conv.	−2.3		
K	helicon	−4.946	1 electron	−4.944
	conv.	−4.7		
Rb	conv.	−5.6	1 electron	−6.04
Cu	conv.	−0.6	1 electron	−0.82
Ag	conv.	−1.0	1 electron	−1.19
Au	conv.	−0.8	1 electron	−1.18
Be	conv.	+2.7	—	—
Mg	conv.	−0.92	—	—
Al	helicon	+1.136	1 hole	+1.135
In	helicon	+1.774	1 hole	+1.780
As	conv.	+50.	—	—
Sb	conv.	−22.	—	—
Bi	conv.	−6000.	—	—

it may be not fair to Compare exp. data for hall effect with Drude model and not with FEM.

in the table: FEM → n (no. of Carriers from valena electrons)

examples:

Na: $R_H = -2.619$ exp.

$= -2.603$ FEM

agreement for s-state electrons

Cu: $R_H = -0.6$ exp

$= -0.82$ FEM

⇒ in d-state electrons ⇒ less agreement.

The Sommerfeld Theory of Metals

Reason: d-state electrons do participate in R_H but not totally free.

exap.: for Be $R_H = +2.7$

$= -2.7$ for FEM

not shown in table

The Sommerfeld Theory of Metals

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

☐ Fermi Temperature: T_F:

$$\text{def.}\, T_F = \frac{\varepsilon_F}{k_B} \qquad (2.17)$$

$$\because N = \frac{V}{3\pi^2} k_F{}^3 \qquad (2.12)$$

$$\therefore k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad (2.18)$$

$$\therefore \varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \qquad (2.19)$$

$$\therefore v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad (2.20)$$

$$\therefore T_F = \frac{\hbar^2}{2mk_B}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \qquad (2.21)$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

- ☐ *Here: We want to derive the Fermi-Dirac Distribution function*
- ☐ When we have *N-paricle system* of electrons at T≠ 0, it will be in a steady state where we can average all properties as:

$$\mathrm{P}_N(E) = \frac{e^{-E/K_BT}}{\sum e^{-E_\alpha{}^{\mathrm{N}}/K_BT}} \qquad (2.22)$$

Where P_{N} is the weight function

- ☐ In the newminator we do have the Boltzman factor.
- ☐ $P_N(E)$: the probabliltiy of the system to be in the state E.
- ☐ This formula arises from the postulate that the probability of finding a system in a particular state is proportional to the Boltzmann factor for that state. The partition function in the denominator serves as a normalization factor to ensure that the sum of the probabilities of all possible states is equal to one.

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

- ❑ Here E_α^N is the energy of the αth stationary state of the N-electron system (the sum being over all such states).
- ❑ The denominator of (2.22) is called the partition function, and is related to the Helmholtz free energy. *F = U - TS* (where *U* is the internal energy and S, the entropy) by:

$$\sum e^{-E_\alpha{}^N/K_BT} = e^{-F_N/K_BT} \qquad (2.23)$$

$$(2.22) \rightarrow \mathrm{P}_N(E) = e^{-(E-F_N)/K_BT} \qquad (2.24)$$

- ❑ We have selected the system to be at T≠ 0, so that thermal fluctuations allow the system to explore different energy states.
- ❑ The distribution must be modified to account for the Pauli exclusion principle for Fermions.

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

- Let f_i^N represents the probability of finding an electron in the particular one-electron level *i,* when the N-electron system is in thermal equilibrium.

$$f_i^N = \sum \mathrm{P}_N (E_\alpha^N) \qquad (2.25)$$

$$= 1 - \sum \mathrm{P}_N (E_\gamma^N) \qquad (2.26)$$

- Where the last summation is the summation over all N-electron states γ in which there is *no* electron in the one-electron level *i*.
- We then do the summation over all (*N + 1*)-electron states in which there is an electron in the one-electron level i:

$$f_i^N = 1 - \sum \mathrm{P}_N (E_\alpha^{N+1} - \varepsilon_i) \qquad (2.27)$$

$$= 1 - \sum e^{(\varepsilon_i - \mu)/K_B T} \, \mathrm{P}_{N+1}\left(E_\alpha^{N+1}\right)$$

$$= 1 - e^{(\varepsilon_i - \mu)/K_B T} \sum \mathrm{P}_{N+1}\left(E_\alpha^{N+1}\right) \qquad (2.28)$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

- ❑ where μ, known as the chemical potential, is given at temperature T by:

$$\mu = F_{N+1} - F_N \qquad (2.29)$$

- ❑ Comparing (2.28) with (2.25):

$$f_i^{\,N} = 1 - e^{(\varepsilon_i - \mu)/K_B T} f_i^{\,N+1} \qquad (2.29)$$

- ❑ Equation (2.29) gives an exact relation between the probability of the one electron level *i* being occupied at temperature T in an N-electron system, and in an *(N* + 1)-electron system
- ❑ For large N, $f_i^{N+1} \approx f_i^N$

$$f_i^{\,N} = 1 - e^{(\varepsilon_i - \mu)/K_B T} f_i^{\,N} \rightarrow f_i^{\,N}\left(1 + e^{(\varepsilon_i - \mu)/K_B T}\right) = 1$$

$$\therefore f_i^{\,N} = \frac{1}{e^{(\varepsilon_i - \mu)/K_B T} + 1} \qquad (2.30)$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

❑ In reality, no need for the superscript N, Hence: Fermi-Dirac Function can be written as:

$$f_i = \frac{1}{e^{(\varepsilon_i - \mu)/K_B T} + 1} \qquad (2.30)$$

❑ Total No. of states N is then:

$$N = \sum_i f_i = \sum_i \frac{1}{e^{(\varepsilon_i - \mu)/K_B T} + 1} \qquad (2.31)$$

❑Hence, N depends on T and μ

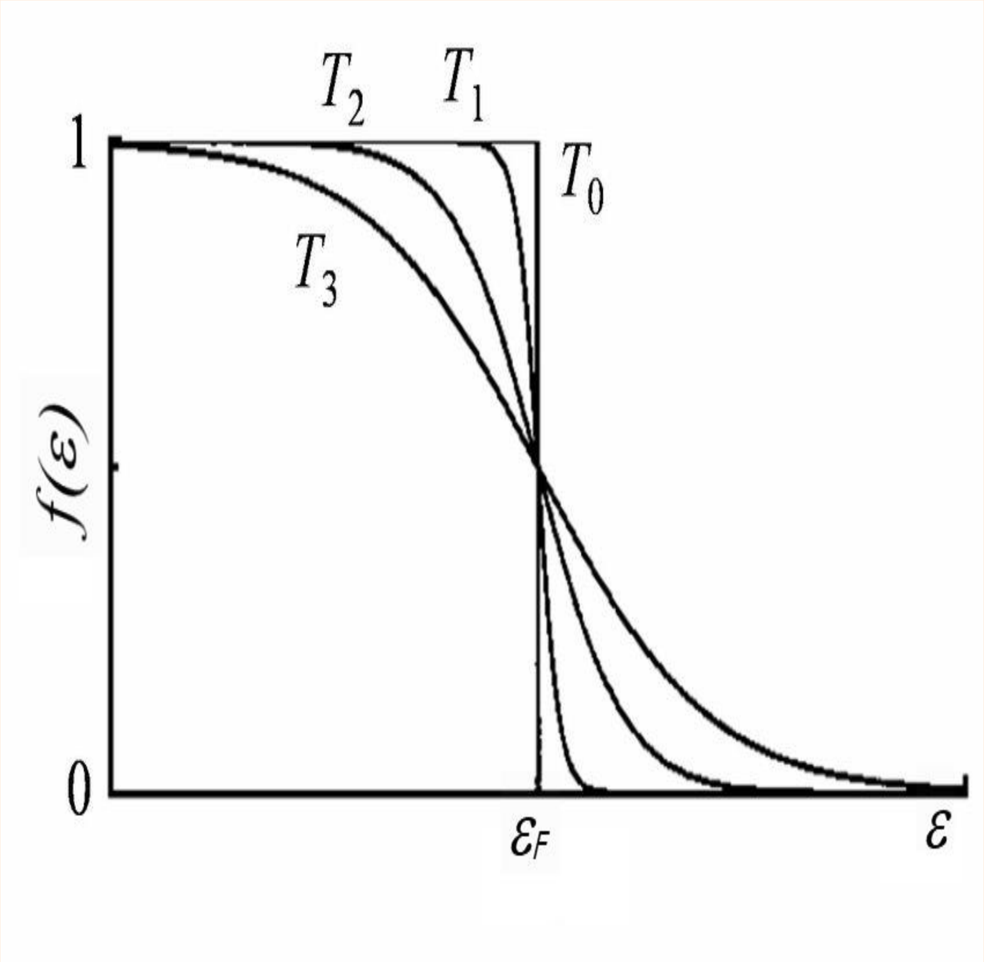
THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

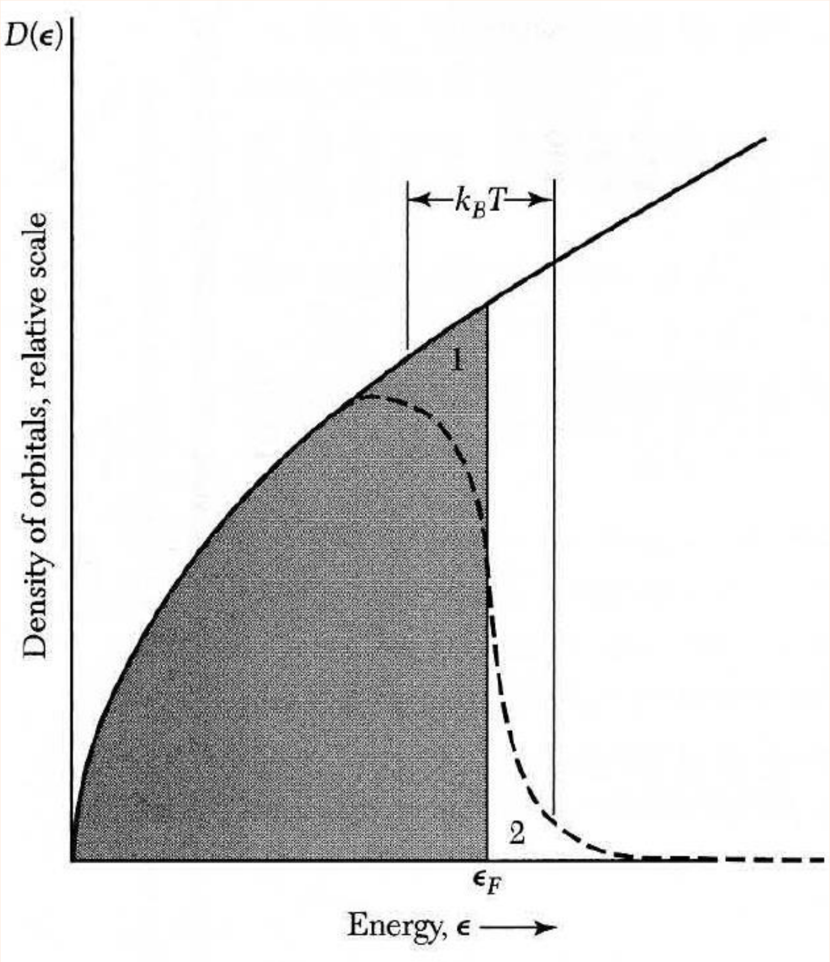
- ☐ We are going to derive an equation of the *heat capacity* based on this statistics.
- ☐ Classical statistical mechanics predicts that a free particle should have a heat capacity of $\frac{2}{3}k_B$.
- ☐ If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $\frac{2}{3}Nk_B$
- ☐ But the observed electronic contribution at room temperature is usually less than 0.01% of this value
- ☐ This important discrepancy distracted the early workers, such as Lorentz: *How can the electrons participate in electrical conduction processes as if they were mobile, while not contributing to the heat capacity?*

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

- ☐ The question was answered only upon the discovery of the Pauli exclusion principle and the Fermi distribution function
- ☐ Fermi found the correct result and he wrote, "*One recognizes that the specific heat vanishes at absolute zero and that at low temperatures it is proportional to the absolute temperature*."
- ☐ When we heat the specimen from 0 K, not every electron gains an energy ~$k_B T$ as expected classically, but only those electrons in orbitals within an energy range $k_B T$ of the Fermi surface are excited thermally.
- ☐ This gives an immediate qualitative solution to the problem of the heat capacity of the conduction electron gas.
- ☐ If N is the No. of electrons, only a fraction of the order of T/T_F can be excited thermally at T, because only these lie within an energy range of the order of $k_B T$ of the top of the energy distribution.

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION





THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

❑ Each of the $N.T/T_F$ electrons has a thermal energy of the order k_BT

❑ The total electronic thermal kinetic energy U is of the order of:

$$U_{el} \approx \frac{NT}{T_F} k_B T \tag{2.32}$$

$$\rightarrow C_{el} = \frac{\partial U_{el}}{\partial T} \approx N k_B \left(\frac{T}{T_F}\right) \tag{2.33}$$

❑ So, it is directly proportional to *T,* in agreement with the experimental results.

❑ We now derive a quantitative expression for the electronic heat capacity valid at low temperatures: $k_BT \ll \varepsilon_F$

❑ The increase $\Delta U = U(T) - U(0)$ in the total energy of a system of *N* electrons when heated from 0 to *T* is:

$$\Delta U = \int_0^\infty \varepsilon d\,\varepsilon D(\varepsilon) f\,(\varepsilon) - \int_0^{\varepsilon_F} \varepsilon d\,\varepsilon D(\varepsilon) \tag{2.34}$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

- f(ε) is the Fermi-Dirac distribution function showed before. And D(ε) is the number of orbitals per unit energy range.

$$f\ (\varepsilon,T\ ,\mu)=\frac{1}{e^{(\varepsilon-\mu)/K_BT}\ +1} \qquad (2.30)$$

$$\because N\ =\int_0^\infty d\,\varepsilon D(\varepsilon)f\ (\varepsilon)=\int_0^{\varepsilon_F} d\,\varepsilon D(\varepsilon) \qquad (2.35)$$

N is the total no. of electrons.

$$(2.31)\times\varepsilon_F\ :$$

$$\int_0^\infty \varepsilon_F d\,\varepsilon D(\varepsilon)f\ (\varepsilon)=\int_0^{\varepsilon_F}\varepsilon_F d\,\varepsilon D(\varepsilon)$$

$$\rightarrow \int_0^{\varepsilon_F}\ \int_{\varepsilon_F}^\infty \varepsilon_F d\,\varepsilon D(\varepsilon)f\ (\varepsilon)=\int_0^{\varepsilon_F}\varepsilon_F d\,\varepsilon D(\varepsilon) \qquad (2.36)$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

❑ Using (2.36) in (2.34):

$$\Delta U = \int_{\varepsilon_F}^{\infty} d\varepsilon(\varepsilon-\varepsilon_F)D(\varepsilon)f(\varepsilon)+\int_{0}^{\infty} d\varepsilon(\varepsilon_F-\varepsilon)\left[1-f(\varepsilon)\right]D(\varepsilon) \qquad (2.37)$$

❑ The first integral on the right-hand side of (2.37) gives the energy needed to take electrons from ε_F to the orbitals of energy $\varepsilon>\varepsilon_F$, and the second integral gives the energy needed to bring the electrons to ε_F from orbitals below ε_F .Both contributions to the energy are positive.

❑ The product *f*(ε)*D*(ε)*d*ε in the first integral of (2.37) is the No. of electrons elevated to orbitals in the energy range *d*ε at an energy ε

❑ The factor [1 - *f*(ε)] in the second integral is the probability that an electron has been removed from an orbital ε.

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

- ☐ The heat capacity is found on differentiating *ΔU* with respect to *T*. The only temperature-dependent term in (2.37) is *f(ε)*

$$C_{el} = \frac{dU}{dT} = \frac{d}{dT}\left[\int_{\varepsilon_F}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon - \int_{0}^{\infty}(\varepsilon-\varepsilon_F)\left[1-f(\varepsilon)\right]D(\varepsilon)d\varepsilon\right]$$

$$= \frac{d}{dT}\left[\int_{\varepsilon_F}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon - \int_{0}^{\infty}\varepsilon D(\varepsilon)d\varepsilon + \int_{0}^{\infty}\varepsilon_F D(\varepsilon)d\varepsilon + \int_{0}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon\right]$$

$$= \frac{d}{dT}\left[\int_{\varepsilon_F}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon + \int_{0}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon\right]$$

$$= \frac{d}{dT}\left[\int_{0}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon\right]$$

$$C_{el} = \left[\int_{0}^{\infty}(\varepsilon-\varepsilon_F)\frac{\partial f(\varepsilon)}{\partial T}D(\varepsilon)d\varepsilon\right] \qquad (2.38)$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

❑ By approximating D(ε) ≈ D(ε_F):

$$C_{el} \approx D(\varepsilon_F)\int_0^\infty (\varepsilon-\varepsilon_F)\frac{\partial f(\varepsilon)}{\partial T}d\varepsilon \qquad (2.39)$$

$$\because k_BT << \varepsilon_F \rightarrow \mu \approx \varepsilon_F$$

$$\therefore \frac{\partial f(\varepsilon)}{\partial T} = \frac{\partial}{\partial T}\frac{1}{e^{(\varepsilon-\varepsilon_F)/K_BT}+1}$$

$$= \frac{(\varepsilon-\varepsilon_F)}{(k_BT)^2}\frac{e^{(\varepsilon-\varepsilon_F)/K_BT}}{\left[e^{(\varepsilon-\varepsilon_F)/K_BT}+1\right]^2} \qquad (2.40)$$

$$\text{let}: x = \frac{\varepsilon-\varepsilon_F}{k_BT} \qquad (2.41)$$

$$\therefore C_{el} = k_B^2TD(\varepsilon_F)\int_{-\frac{\varepsilon_F}{K_BT}}^{\infty} x^2\frac{e^x}{(e^x+1)^2}dx \qquad (2.42)$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

- We may replace the lower limit by $-\infty$ because the factor e^X in the integrand is already negligible at $x = -\varepsilon_F/k_BT$

$$\int_{-\infty}^{\infty} x^2 \frac{e^x}{\left(e^x+1\right)^2} dx = \frac{\pi^2}{3} \qquad (2.43)$$

$$\therefore C_{el} = \frac{1}{3}\pi^2 D(\varepsilon_F)\,\mathrm{k}_B^2\, T \qquad (2.44)$$

$$\varepsilon = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad (2.19) \Rightarrow N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}$$

$$\because D(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{3}{2}.\frac{V}{3\pi^2}.\left(\frac{2m}{\hbar^2}\right)^{3/2}(\varepsilon)^{1/2} = \frac{3}{2}.\frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}.\frac{\varepsilon^{1/2}}{\varepsilon^{3/2}}$$

$$\therefore D(\varepsilon) = \frac{3}{2}\frac{N}{\varepsilon} = \frac{3}{2}\frac{N}{K_B T_F}$$

$$\therefore C_{el} = \frac{1}{2}\left(\pi^2 \frac{T}{T_F}\right) N k_B \qquad (2.44)$$

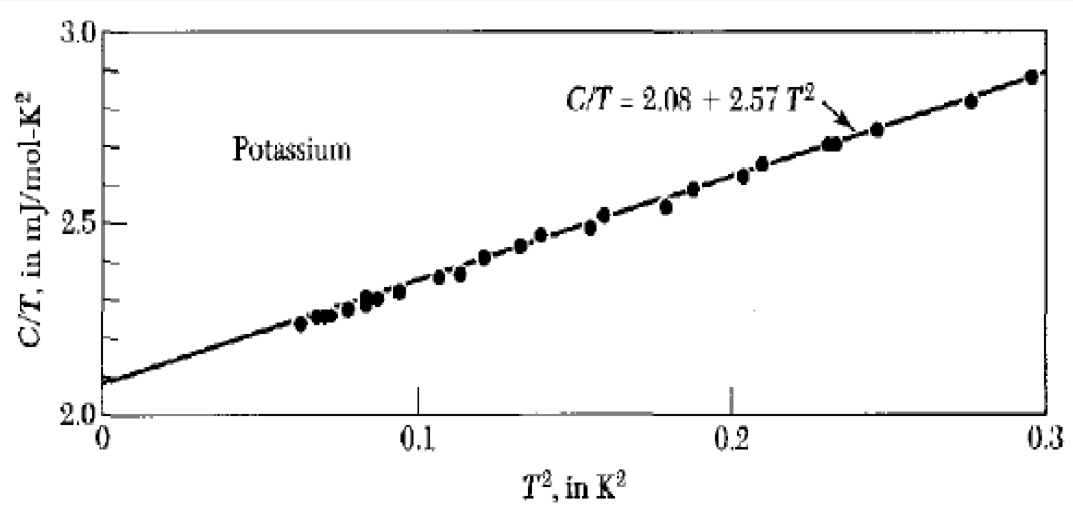
THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

- Hence, C_{el} or C_v is linear in T.
- The prediction of a linear specific heat is one of the most important consequences of Fermi-Dirac statistics. The general form of heat capacity is:

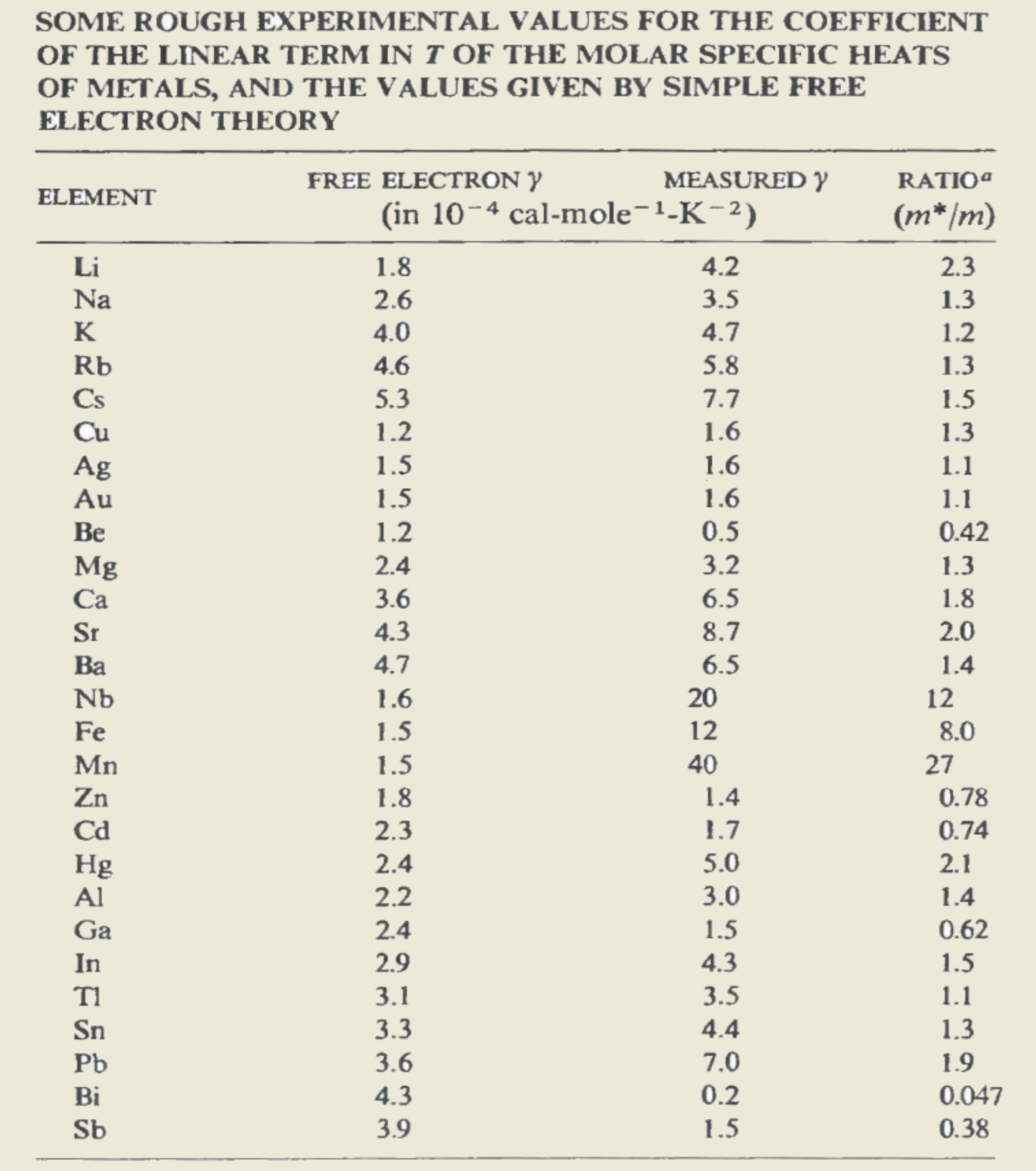
$$C_v = \gamma T + AT^3 \tag{2.45}$$

$$\therefore \frac{C_v}{T} = \gamma + AT^2 \tag{2.46}$$

One can thus find γ by extrapolating the C/T curve linearly down to $T^2 = 0$, and noting where it intercepts the C/T -axis



The Sommerfeld Theory of Metals



SOME ROUGH EXPERIMENTAL VALUES FOR THE COEFFICIENT OF THE LINEAR TERM IN T OF THE MOLAR SPECIFIC HEATS OF METALS, AND THE VALUES GIVEN BY SIMPLE FREE ELECTRON THEORY

ELEMENT	FREE ELECTRON γ (in 10^{-4} cal-mole^{-1}-K^{-2})	MEASURED γ (in 10^{-4} cal-mole^{-1}-K^{-2})	RATIO[a] (m^*/m)
Li	1.8	4.2	2.3
Na	2.6	3.5	1.3
K	4.0	4.7	1.2
Rb	4.6	5.8	1.3
Cs	5.3	7.7	1.5
Cu	1.2	1.6	1.3
Ag	1.5	1.6	1.1
Au	1.5	1.6	1.1
Be	1.2	0.5	0.42
Mg	2.4	3.2	1.3
Ca	3.6	6.5	1.8
Sr	4.3	8.7	2.0
Ba	4.7	6.5	1.4
Nb	1.6	20	12
Fe	1.5	12	8.0
Mn	1.5	40	27
Zn	1.8	1.4	0.78
Cd	2.3	1.7	0.74
Hg	2.4	5.0	2.1
Al	2.2	3.0	1.4
Ga	2.4	1.5	0.62
In	2.9	4.3	1.5
Tl	3.1	3.5	1.1
Sn	3.3	4.4	1.3
Pb	3.6	7.0	1.9
Bi	4.3	0.2	0.047
Sb	3.9	1.5	0.38

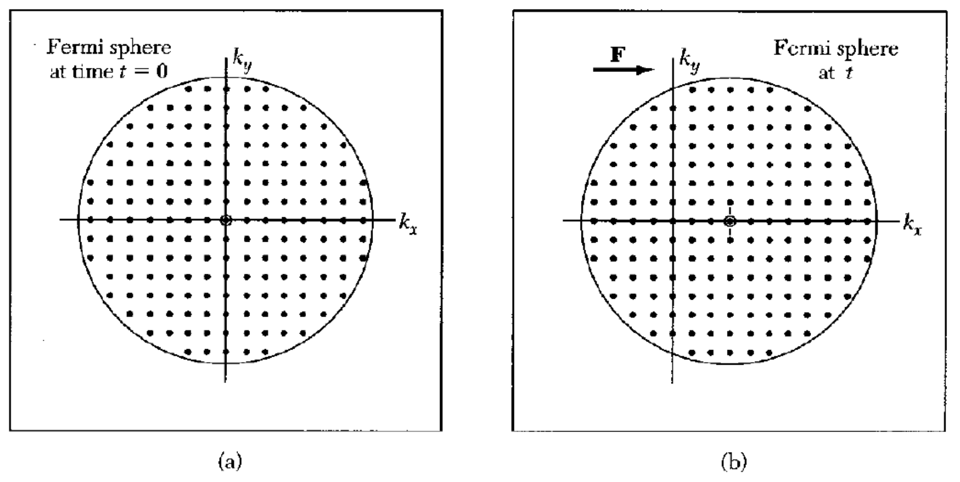
Sommerfeld Theory of Conduction in Metals

- ❑ To find the velocity distribution for electrons in metals, consider a small volume element of k-space about a point **k,** of volume *dk*
- ❑ The number of one-electron levels in this volume element is (from 2.10) with the twofold spin degeneracy in consideration:

$$\left(\frac{V}{4\pi^3}\right)d\mathbf{k} \qquad (2.47)$$

- ❑ The probability of each level being occupied is just *f(ε)*
- ❑ therefore the total number of electrons in the k-space volume element is:

$$\left(\frac{V}{4\pi^3}\right)f\ (\varepsilon)d\mathbf{k} \qquad (2.48)$$



(a) (b)

Sommerfeld Theory of Conduction in Metals

- ❑The velocity of a free electron with wave vector **k** is $\boldsymbol{v} = \hbar\boldsymbol{k}/m$
- ❑ the number of electrons in an element of volume dV about $\boldsymbol{v}$ is the same as the number in an element of volume: $d\boldsymbol{k} = (m/\hbar)^3 d\boldsymbol{v}$
- ❑ Consequently the total number of electrons per unit volume of real space in a velocity space element of volume dV about $\boldsymbol{v}$ is: $f(\boldsymbol{v})d\boldsymbol{v}$ with:

$$f\,(v\,) = \frac{\left(m\,/\,\hbar\right)^3}{4\pi^3}\frac{1}{\exp\left[\left(\frac{1}{2}mv^{\,2} - \mu\right)/\,k_{\,B}T\,\right]+1} \qquad (2.49)$$

- ❑Sommerfeld reexamined the Drude model, replacing the classical Maxwell-Boltzmann velocity distribution (2.1) by the Fermi-Dirac distribution (2.49).

Sommerfeld Theory of Conduction in Metals

❑Fermi velocity can be derived as:

$$\because v = \frac{\hbar k}{m}$$

$$\therefore v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad (2.50)$$

$$\because \ell = v_F \tau$$

$$\therefore \ell = \frac{\hbar \tau}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad (2.50)$$

❑ This is the mean free path of electrons

Thanks